

Distribution and Fluxes of Total and Methylmercury in Lake Superior

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Despite the importance and size of Lake Superior, little is known regarding the biogeochemical cycling or distribution of mercury within its waters. We present the results from two research cruises on total Hg (HgT) and methylmercury (MeHg) distributions in aqueous and particulate phases, and in offshore sediments. Open waters of Lake Superior are similar in HgT content to Lakes Michigan and Ontario (sub- $\mu\text{g L}^{-1}$), whereas MeHg was only 1% of HgT. Seasonality in aqueous HgT distribution was observed, most likely from tributary inputs during Spring snowmelt. Suspended particles were enriched in MeHg relative to water and surficial sediments, suggesting enhanced particle partitioning followed by demethylation in the water column and in surface sediments. Distribution coefficients for mercury in surficial sediments were lower than those in suspended material, likely due to remineralization. Preliminary estimates of mass balance indicate that air–water exchange processes such as evasion and wet deposition dominate the HgT budget, due to the basin's relatively small watershed area relative to lake area. In contrast, methylmercury cycling within Lake Superior is influenced more strongly by watershed sources, as well as by sedimentary sources and photodemethylation. The Hg cycle in Lake Superior is unique in that it is more similar in many aspects to that in marine systems than in small lakes, where management data for freshwaters typically originates.

Introduction

Methylmercury (MeHg) is a potent human and wildlife neurotoxin that readily bioaccumulates in the aquatic food web and diminishes the commercial, nutritional, and cultural value of fishery resources within impacted systems (1). Methylmercury contamination has led to fish consumption advisories in 41 states throughout the U. S., including those neighboring the Lake Superior Basin (2) and Ontario (3).

Such advisories exist for the lake itself, targeting sport fish such as lake trout and walleye (2, 4). Nearshore zones are of particular interest, where MeHg supply from tributaries and potential in situ production in shallow sediments may enhance biological uptake (5, 6). The majority of fish species in Lake Superior (43 of 48) either spawn or spend a significant portion of their early life history in these regions (7).

Despite the risks associated with MeHg contamination in Lake Superior fish, little is known about mercury speciation, distribution, or fluxes in the lake, and its potential for harmful exposure to resident human and fish-eating wildlife populations. To date, only one study using "clean techniques" for sampling and analyses determined total Hg (HgT) in surface water of Lake Superior ($\sim 0.5 \text{ ng L}^{-1}$; ref 8). Data on other trace metal distributions in the Great Lakes were summarized in Nriagu et al. (9).

Although analyses of HgT in offshore waters suggest that levels are quite low relative to those of other freshwater systems, the issuance of numerous fish consumption advisories indicates that MeHg has been formed and bioaccumulated in the food chain. Methylmercury production results from an array of biological, physical, and chemical processes that interact under very specific environmental conditions. Mercury supply to the Lake Superior Basin is thought to be driven primarily by human activity, via emission and subsequent wet and dry atmospheric deposition as Hg(II) and MeHg (10–12). Such deposition occurs directly to the lake, as well as to its surrounding watershed. Regional land use (e.g., agricultural, urban), land cover characteristics (e.g., wetlands, forest, surficial geology), and preliminary data on Hg in tributaries (5, 6, 13) strongly suggest that watershed formation and transport of MeHg is an important source to the lake.

On the basis of our prior work on Lake Superior tributaries and collections of atmospheric deposition (13, 14), we hypothesize that atmospheric loading is the dominant source of HgT to the lake. These preliminary measurements also suggest that direct atmospheric deposition and tributary input of MeHg are of similar magnitude. This is due in part to the relatively small watershed/lake area ratio, which emphasizes the importance of wet and dry direct deposition. Large uncertainties remain, however, including the contribution of near-shore and deep sediment MeHg produced in situ from microbial methylation.

The relatively few studies that have characterized HgT and MeHg in the Great Lakes indicate that aqueous concentrations are low relative to those in small inland lakes and other fresh waters. Mason and Sullivan (15) reported that concentrations of Hg species in the Lake Michigan water column were comparable to open ocean concentrations (sub- $\mu\text{g L}^{-1}$), and presented a mass balance indicating that water column and particulate Hg concentrations did not vary significantly in space or time. Quemerais et al. (16) reported similar HgT concentrations near the outlet of Lake Ontario.

This research was conducted as part of a larger U.S. EPA STAR-funded study investigating the controls on Hg speciation and bioavailability within the Lake Superior Basin. Our objectives were (1) to determine the spatial/temporal speciation and distribution of mercury species in Lake Superior, (2) to determine the principal sources of MeHg and Hg(II) to the lake, and (3) to quantify processes that control its fate and transport. We present the first comprehensive data on aqueous Hg speciation and distribution for offshore regions of the lake, and present a preliminary mass balance.

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TABLE 1. Hg Speciation in Lake Superior Water Column, August 2000

site	lat N	long W	depth m	April 2000 part. MeHg ng g ⁻¹ dw	Aug 2000 part. MeHg ng g ⁻¹ dw	Aug 2000 aq MeHg pg L ⁻¹	Aug 2000 MeHg log Kd L kg ⁻¹	Aug 2000 part. HgT ng g ⁻¹ dw	Aug 2000 aq reactive Hg pg L ⁻¹	Aug 2000 aq DGM pg L ⁻¹
1	46° 59.58"	85° 09.73"	10	4.7	3.3	7.6 ± 2.1	5.6		21 ^b	32
2	47° 21.74"	85° 37.29"	10	0.4	4.8	4.3 ± 0.1	6.1		113	23
3	46° 53.64"	85° 51.14"	10	6.3 (2.5, 10.2)	3.5	3.5 ± 0.4	6.0	29.9	71	
4	47° 15.61"	86° 20.70"	10	2.5	1.7			49.3	29 ^b	
			114	4.0	0.6			21.4		
6	48° 33.39"	86° 22.71"	10	5.7	3.0	6.1 ± 1.2	5.7	79.2	61	6 ^b
			142	0.02 ^b	3.6	12.6	5.5		23 ^b	
7	48° 04.35"	86° 35.38"	10	0.01 ^b	3.5	7.5 ± 0.8	5.7		42	6 ^b
8	47° 36.35"	86° 49.23"	10	0.01 ^b		4.0		45.5	28 ^b	
10	47° 30.62"	87° 33.00"	10	2.7	2.0	3.5 ± 0.9	5.7	73.9	90	
			130	2.0	2.6	6.6 (5.4, 7.7)	5.6	8.7	90	6 ^b
11	48° 20.57"	87° 49.70"	10	11.7	3.1 (2.7, 3.6)	4.8 ± 0.3	5.8		23 ^b	19 (16, 22)
14	47° 44.46"	88° 44.26"	10	3.5	1.4	5.9 (3.7, 8.1)	5.4	49.2	58	34 (33, 34)
15	48° 04.84"	89° 15.24"	10	3.0	0.9	7.0 ± 3.1	5.1	42.7	18 ^b	16 (13, 19)
			222	14.5	1.5	5.3 (4.8, 5.8)	5.5	15.2	17 ^b	
17	47° 09.74"	89° 39.74"	10	4.7	5.1 (3.6, 6.5)	3.0 ± 0.5 ^b	6.2		109	12 (11, 12)
			163	0.8						
18	47° 30.85"	90° 08.93"	10	19.4	6.8	4.4 ± 0.9	6.2	24.5 (20.0, 29.1)	65	22
19	47° 22.23"	90° 51.12"	10	4.8	1.0				83	
20	46° 52.93"	90° 16.90"	10		3.2	4.6 (4.2, 4.9)	5.8		38	
			96		4.8	1.6 ^b (1.2, 2.0)	6.5			
21	47° 09.63"	87° 47.38"	10		1.5			86.2	51	19
			93		3.5			65.3	22 ^b	27
22	46° 48.19"	91° 45.03"	44		5.6	12.8	5.6	15.0	16 ^b	34
mean ± se				4.8 ± 1.2	3.0 ± 0.4	5.8 ± 0.7	5.8 ± 0.1	43 ± 7	51 ± 7	20 ± 3

^a Results are presented as mean ± SE of triplicate samples, (#) = range of duplicate samples. ^b Below method detection limit.

Study Region

Lake Superior is the world's largest freshwater lake by surface area (8.21×10^4 km²), and third largest by volume (1.21×10^4 km³), and has average and maximum depths of 147 and 406 m, respectively. The Lake Superior watershed area (1.27×10^5 km²) is only about 1.5 times the size of its lake area, presumably placing a greater emphasis on direct atmospheric deposition of pollutants than in other systems (17). The basin is sparsely populated, yet it has received a significant amount of historical contamination from mining and industrial activities within the basin (paper manufacture, mining, chlor-alkali production) and from natural geological deposits (4, 18, 19).

Much of Lake Superior remains well mixed throughout the year, with thermal stratification along shorelines and sporadic weak stratification offshore (20). Seasonality is not observed in major ion distributions, nor does the hypolimnion become anoxic at depth (21). Surface water temperatures rarely exceed 15 °C, and generally only seasonally along the far southern shore and its associated bays. Such shallow coastal zones are potential sites for enhanced seasonal in situ methylation in surficial sediments.

Methods

Water and Suspended Particulates. Samples were collected from April 22 to 29 and August 22 to 29, 2000 from the U.S. EPA vessel *R/V Lake Guardian*. Sampling was conducted concurrently with the EPA Great Lakes National Program Office's water sampling monitoring program (Table 1; ref 20). Sampling was conducted to seasonally characterize Hg speciation in the water column. Twenty stations were sampled in April, and 21 sites were sampled in August. Additional depths and samples were collected at several "master" sites in order to highlight regions of Lake Superior that are characteristic of human impact [e.g., stations 6 (Wawa, Ontario), 15 (Thunder Bay, Ontario), and 22 (Duluth-Superior, MN-WI)], coastal, and open-lake zones (Table 1, Figure 1). "Master" sites consisted of collection of water and particles from surface (10 m) and bottom (20 m above sediment-water interface) depths, as well as size fraction-

ation of surface water particles, collections of surface water zooplankton (22), surficial sediment grab samples, intact sediment cores, and benthic organisms. "Nonmaster" sites were sampled for water and particulate Hg only at 10 m depth. Unfiltered HgT and particle-bound MeHg were collected during April and August, whereas additional Hg species [unfiltered MeHg, dissolved gaseous Hg, reactive Hg(II)] were collected in August only. Ancillary measures of dissolved organic carbon (DOC), absorbance at 254 nm, and suspended particulate matter (SPM) were determined for both cruises. Dissolved organic carbon was measured with a Shimadzu TOC-5000 analyzer; absorbance was measured by a Hewlett-Packard 8452A UV-Visible spectrophotometer; and SPM determination was by filtration through 0.40-μm polycarbonate membranes followed by mass determination with a Perkin-Elmer AD-4 microbalance.

Water samples were collected using acid-cleaned, Teflon-lined, 12-L Go-Flo bottles (General Oceanics Co.) attached to Kevlar hydrowire, and tripped at depth with a Teflon-coated messenger. Water samples were immediately decanted into acid-cleaned 2-L Teflon bottles for storage until subsequent processing or analysis. Concurrent ancillary water data were collected by the *R/V Lake Guardian* EPA crew by Niskin bottle and CTD array, including station position, temperature, depth, conductivity, turbidity, particulate matter, and chlorophyll content (20).

Water samples for HgT analysis were acidified upon collection to 1% v/v HCl (trace metal grade), and stored until analysis. All other Hg analytes were determined within 6 h of collection aboard the *R/V Lake Guardian*. Total Hg was determined using standard techniques (23, 24), including preoxidation by BrCl, reduction by NH₂OH·HCl and SnCl₂, preconcentration of Hg⁰ onto a Au trap with an aspirator, and analysis by cold vapor atomic fluorescence spectrophotometry (CVAFS) with a Tekran model 2500 detector. Reactive Hg was determined within 1 h of collection by addition of SnCl₂ to unfiltered, unacidified samples, followed by the purge/trap CVAFS method. Dissolved gaseous Hg was determined within 1 h of collection by purging unfiltered samples with N₂ through a soda lime column and two Au

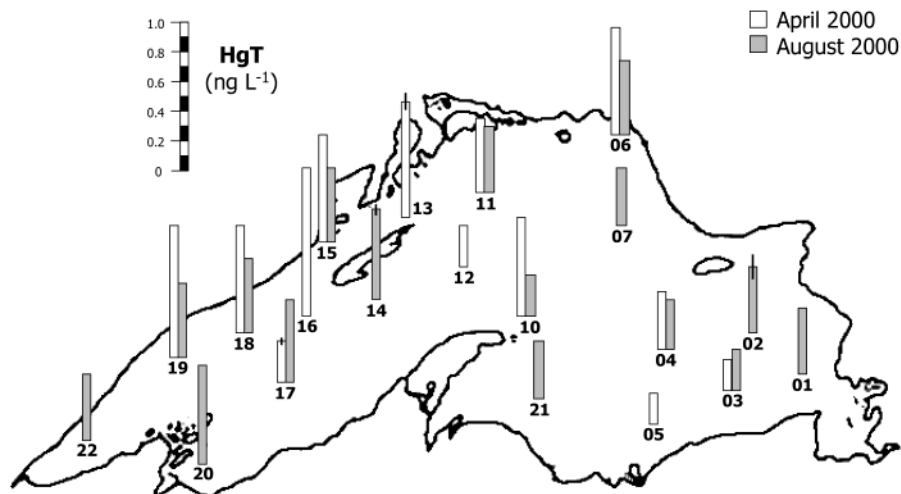


FIGURE 1. Summary of HgT content (ng L^{-1}) in unfiltered surface waters (10 m depth) collected in April and August 2000. Numbers below bars are station IDs. Error bars, where shown, are standard error of the mean.

traps in series (to assess trap efficiency), using the methods of Rolffhus and Fitzgerald (25).

We were unable to detect ambient MeHg concentrations in Lake Superior in April 2000 by using the standard distillation–ethylation–GC separation–CVAFS techniques ($\text{MDL} = 30 \text{ pg L}^{-1}$; refs 24, 26), so we modified the technique to a large-volume direct ethylation procedure for ship-board measurement in August 2000. Unfiltered water samples (850 mL) were decanted into a 1-L aspirator, with the addition of 1.4 mL of 20% w/v acetate buffer (pH 4.8), and 0.2 mL of 1% w/v sodium tetraethylborate. The mixture reacted for 25 min, followed by purge/preconcentration onto a Carbotrap for 30 min at 0.5 L min^{-1} , drying of carbotraps for 10 min, and analysis by the standard GC–CVAFS procedure. The method detection limit for this modified technique was 3.1 pg L^{-1} . The direct ethylation technique may potentially underestimate aqueous MeHg content in unfiltered samples, as particles may consume the ethylating reagent; thus, our values should be interpreted as an operationally defined fraction rather than “total” MeHg.

Clean, ashed quartz fiber disks were used for collecting suspended particulate matter for HgT and MeHg analysis. A Teflon filter tower (Saville Co.) was attached to an acid-cleaned desiccator under a ship-board HEPA filter, with the collection bottle placed inside; vacuum was applied to the desiccator using a small piston pump. Loaded filters were immediately placed into Teflon Petri dishes, and kept frozen and dark until analysis. Total Hg in particles was determined by placing the loaded filter into a 125-mL Teflon bottle, adding 100 mL of deionized water and 4 mL of BrCl, digesting for 12 h at 40°C , and analyzed as per aqueous samples. Methyl Hg in particles was determined by placing the filter into a 125-mL Teflon bottle, adding 100 mL of water, 1 mL of 50% v/v H_2SO_4 , 1 mL of 1 M CuSO_4 , and 0.5 mL of 1 M KCl, and then steam distilled into Teflon jars for approximately 5 h (85% of the volume). Distillates were analyzed using the modified ethylation–GC separation–CVAFS technique described in Olson et al. (24) and Horvat et al. (26).

Sediments. Intact sediment cores were obtained from a 0.25 m^2 box corer. Cores were manually collected from the top of the box, as 4-cm i.d. acrylic core barrels were gently inserted to at least 10 cm depth. Cores for stratigraphic profiling and porewater Hg content were collected at eight and four stations, respectively, in August 2000. Stratigraphic cores were sectioned into 1- or 2-cm intervals using an acrylic extruder and polypropylene collection cups, and samples were immediately frozen until analysis. Sediment porewater was obtained by squeezing the contents of the core barrel

with adjustable Teflon pistons (27, 28) until liquid flowed through tubing mounted at discrete intervals on the core side and into 30-mL Teflon bottles. Typically only 5–10 mL was obtained for HgT and MeHg analysis per 2-cm interval using the squeezing technique. Porewater was immediately acidified to 1% HCl v/v, and stored cold until analysis.

Solid-phase HgT was determined by adding 0.2 g of lyophilized sediment to a Teflon threaded jar, with the addition of 15 mL of a 2:5 v/v mixture of trace metal grade $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture, and 10 mL of deionized water. Samples were microwave-digested, followed by the addition of 1 mL of BrCl, and further digestion at 40°C for 12 h. Total Hg was determined with analytical methods similar to that of aqueous samples. Methyl Hg was determined in solid-phase samples using the modified steam distillation–ethylation–GC separation–CVAFS procedures described in Olson et al. (24).

Quality Assurance. Method detection limits for aqueous HgT, MeHg, HgR, and DGM were 68, 3.1, 33, and 7.3 pg L^{-1} , respectively. Detection limits for HgT and MeHg in solids were 2.5 and 0.03 ng g^{-1} dry weight, respectively. The coefficient of variation for the low-level MeHg analysis replicates averaged 29% for 11 samples. Field replicates were analyzed for 10% of all aqueous samples, and field blanks for aqueous HgT collections were generally less than 20% ($<0.1 \text{ ng L}^{-1}$) of the mean ambient concentration. Analytical duplicates were analyzed for all HgT samples, with acceptance at or less than 10% relative percent difference (RPD). Ten percent of all MeHg samples were distilled and analyzed in duplicate to meet our laboratory acceptance criteria, $<25\%$ RPD. Data not meeting these criteria were not included in these datasets. Sample collections included field blanks, standard additions, and use of the National Reference Council Canada standard reference material MESS-2 (marine sediment) for solid-phase samples (mean 93.3 ng g^{-1} dw, certified range $91 \pm 9 \text{ ng g}^{-1}$).

Results and Discussion

Water. Results of HgT in unfiltered fractions of Lake Superior water for both cruises are presented in Figure 1. It is apparent that aqueous unfiltered HgT concentrations are quite low in Lake Superior (mean \pm SE, April 0.57 ± 0.07 , August $0.47 \pm 0.03 \text{ ng L}^{-1}$), but somewhat higher than those observed in Lake Michigan (mean 0.32 ng L^{-1} ; ref 15), filtered HgT in waters exiting Lake Ontario (mean 0.26 ng L^{-1} ; ref 16), and open ocean environments ($0.2\text{--}0.5 \text{ ng L}^{-1}$; refs 29, 30). Concentration gradients were observed in time and space, with the highest values occurring in April, particularly along

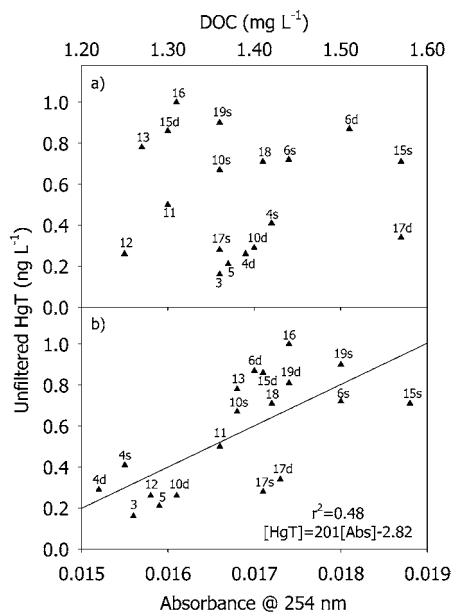


FIGURE 2. Relation between aqueous unfiltered HgT content and (a) DOC content and (b) absorbance at 254 nm, a signature of dissolved organic carbon from terrestrial sources. Accompanying numbers are station IDs: s, surface sample; d, deep sample.

the northwestern shoreline of the lake (Figure 1). Mercury in the particulate fraction averaged 18% of HgT in April and 26% in August, potentially reflecting enhanced particle association during warmer months. Unfiltered HgT concentrations in deep waters averaged 89% and 88% of that in near-surface waters in April and August, respectively, indicating that the water column was relatively well mixed throughout the study period. Mason and Sullivan (15) found a similar well-mixed water column in Lake Michigan, with approximately 36% of the Hg in the particulate phase.

Spatial distributions suggest that near-shore processes are enhancing HgT concentrations in western Lake Superior, likely due to riverine input of elevated HgT water. This contention is supported by the observed positive correlation between unfiltered HgT and absorbance at 254 nm during April 2000 ($r^2 = 0.48$; Figure 2b), despite the relatively small range in bulk DOC concentration (Figure 2a). A strong relationship has been demonstrated between DOC absorptivity in the ultraviolet region, aromaticity, and average molecular weight, which are indicators of terrestrially derived DOC (31). Strong correlation of HgT with bulk DOC was not observed, suggesting that a substantial amount of Hg enters the lake bound to high-molecular-weight DOC from riverine sources. For example, surface water at station 19 (sample 19s) was similar in bulk DOC content to station 17s, but was much higher in HgT concentration (Figure 2a). This may be potentially explained by changes in terrestrial DOC content (Abs 254) between these stations (Figure 2b). Further, whereas stations 17s and 17d share similar Abs 254 characteristics versus HgT, the bulk DOC reflects a contribution of low-HgT DOC at depth (Figure 2a). Generally, the offshore and eastern Lake Superior stations exhibited relatively low 254-nm absorbance values. Elevated HgT was not observed along the northwest shore during the August 2000 sampling, when the lake received lower flows from tributaries. These data contrast with those for Lake Michigan, where no significant horizontal or vertical trends were observed over time, with the exception of particle dynamics related to diatom blooms, fall mixis, and storms (15). Similar seasonal increases may not be observed in Lake Michigan due to the watershed characteristics that dictate tributary DOC and Hg levels. Lake

Superior's watershed is dominated by forested and wetland watersheds, whereas the Lake Michigan basin is dominated by agricultural, and to a lesser extent, forested watersheds (32).

The MeHg content in unfiltered Lake Superior waters during August 2000 was quite low (Figure 3; surface mean $5.1 \pm 0.9 \text{ pg L}^{-1}$, deep $7.8 \pm 2.2 \text{ pg L}^{-1}$), with $27 \pm 5\%$ associated with the particulate phase. Per-volume MeHg concentrations in the particulate phase (Figure 3) were calculated by multiplying the particulate concentration (ng g^{-1}) by measures of suspended particulate matter content, whereas dissolved MeHg is obtained by difference from the whole water concentration. Overall, MeHg accounted for just 1.1% of HgT on a per-volume basis. These values are somewhat lower than those observed in Lake Michigan in 1994, with unfiltered concentrations of $13.5 \pm 4.7 \text{ pg L}^{-1}$ and 4% of the HgT value (15). Similar to HgT, the highest MeHg levels were observed near-shore in the northern and western regions of the lake, while the offshore areas exhibited consistently lower values. We suggest that near-shore sediments and tributaries are supplying MeHg to the water column, where it is slowly scavenged by settling particles or decomposed by photodegradation. Concentrations of MeHg in tributary waters during high flow periods associated with Spring snowmelt can easily exceed 200 pg L^{-1} (5, 33), concentrations much higher than those observed in offshore regions of Lake Superior. We therefore suggest that tributary mixing zones are also important regions for uptake of this bioaccumulative form of mercury (6).

Reactive Hg(II) (HGR minus DGM) averaged $54 \pm 8 \text{ pg L}^{-1}$ (10% of HgT) in unfiltered surface waters, which is at the lower end of the range observed for small seepage lakes in Wisconsin (10–40%; refs 10, 34). Dissolved gaseous Hg averaged $20 \pm 3 \text{ pg L}^{-1}$ in unfiltered surface waters (3.6% of HgT; 300% saturated relative to atmospheric equilibrium), which is similar to that found for Lake Michigan (28 pg L^{-1} ; ref 15). Individual measures of DGM did not correlate with observations of photosynthetically active radiation taken by the *R/V Lake Guardian* CTD array, suggesting that measurements may be reflective of cumulative effects of gas exchange and Hg^0 production rates (25). Such measures were only weakly correlated with solar radiation flux in Lake Ontario surface waters (35).

Particulate Material. Total suspended particulate mass did not vary between April (0.36 mg L^{-1}) and August 2000 (0.37 mg L^{-1}), expressed as the mean of all surface and deep stations. Total Hg on particles averaged $43 \pm 7 \text{ ng g}^{-1}$ dry weight, which is lower than that reported for Lake Michigan ($74\text{--}220 \text{ ng g}^{-1}$; ref 15) and water exiting Lake Ontario (220 ng g^{-1} ; ref 16). No distinct spatial difference was observed between coastal and open lake areas during the August 2000 sampling. Distribution coefficients (K_d , L kg^{-1}), presented as the logarithm of the ratio of particulate and aqueous Hg concentrations, averaged 4.8 ± 0.1 for HgT, which is lower than that in Lake Michigan (mean $\log K_d = 5.7$) and its tributaries ($\log K_d = 5.0\text{--}6.9$; ref 32).

Particulate MeHg concentrations (average $3.8 \pm 0.6 \text{ ng g}^{-1}$; $n = 38$) were similar to those observed in Lake Michigan in late 1994 (average 4.1 ng g^{-1} ; ref 15). Particles collected in April contained more MeHg on a dry-weight basis than those collected in August. This may be due to a number of influences, including the delivery of enriched particles from the watershed during peak flow in the Spring, enhanced particle partitioning of MeHg delivered in a dissolved phase during snowmelt, or the relative differences in particle type or algal species present in Spring. Particulate dilution of the MeHg pool was not occurring, as SPM (overall particle mass) did not vary between our April and August collections. Decreased particulate MeHg during the summer may be due to enhanced photodemethylation (36–38) as solar radiation

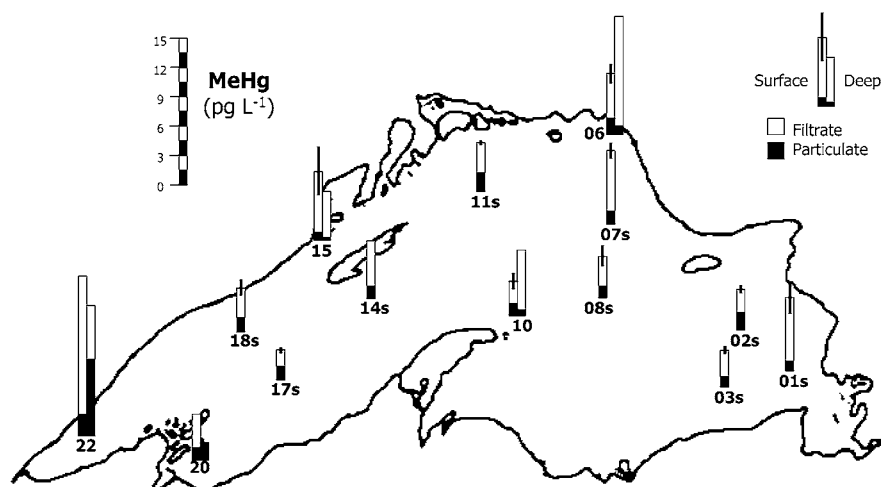


FIGURE 3. Summary of particulate and 0.4- μm filter-passing MeHg content (pg L^{-1}) in the surface and deep waters of Lake Superior during August 2000. Per-volume MeHg concentrations in the particulate phase were calculated by multiplying the particulate concentration (ng g^{-1}) by measures of suspended particulate matter content, whereas dissolved MeHg is determined by difference from the whole water concentration. The particulate component for the surface waters of stations 8 and 22 are estimated on the basis of data from neighboring stations. Numbers below bars are station IDs: s, surface station. Error bars are standard error of the mean.

becomes more intense, or to increased rates of sedimentation of plankton and detritus (17).

The spatial distribution of particulate MeHg was not as distinct as that of aqueous HgT. Generally, the lowest values are observed in the east-central portion of the lake (stations 4 and 10), with higher values nearest the shore. Southern shoreline stations are regions with a high proportion of clay sediments with low MeHg content relative to other sites (33). Only weak gradients of increasing MeHg versus depth are observed at stations where surface and bottom samples were collected. Preliminary evidence suggests that methylation rates in offshore surficial sediments are extremely low relative to more productive systems (incubated cores spiked with stable isotopic Hg(II); ref 14), and that particulate MeHg in deep zones is principally derived from transport from the epilimnion rather than by in situ production. Distribution coefficients for MeHg in Lake Superior particulate matter averaged 5.8 ± 0.1 during August 2000, which is similar to that observed in Lake Michigan ($\log K_d = 5.7$; ref 15).

Sediments. Total and methyl Hg concentrations in surficial sediments (0–2 cm) collected in August 2000 averaged $83 \pm 12 \text{ ng g}^{-1}$ dry weight (dw) and $0.21 \pm 0.03 \text{ ng g}^{-1}$ dw, respectively (Table 2). The mean HgT value is somewhat lower than that reported for 31 Lake Superior stations in 1983 (140 ng g^{-1}) by Rossman (4), though within the range of their study (74 – 180 ng g^{-1}). Rossman's sites were targeted to describe depositional zones of the lake, whereas our study sites were reflective of U.S. EPA surface water survey sites. In 2000, HgT concentrations in bulk sediment were about twice those in suspended particulate material, suggesting that sediment focusing and remineralization/scavenging cycles near the sediment–water interface may be enhancing Hg concentrations in bulk sediment. Methylmercury content in the 0–2 cm interval of the August 2000 sediment cores ($0.21 \pm 0.03 \text{ ng g}^{-1}$) was less than 10% of that observed in suspended matter collected at 10 m depth ($3.0 \pm 0.4 \text{ ng g}^{-1}$), a pattern which may have resulted from demethylation in surficial sediments and/or the nepheloid layer during transport and burial.

Stratigraphic profiles of HgT in sediment cores indicate generally stable or decreasing concentration with depth (Table 2). Two stations (15 and 21) showed sharp decreases in HgT down-core at approximately 5–6 cm. This is consistent with profiles observed by Rossman (4), which typically showed concentration maxima in the 0–4 cm interval. Methylmercury concentrations showed maxima at the top

of the core, indicative of recent particulate settling (followed by demethylation with burial) and, likely to a lesser extent, in situ methylation of Hg(II).

Sediment porewaters were enriched in HgT (mean 31.4 ng L^{-1}) and MeHg content (0.72 ng L^{-1} ; Table 2) relative to overlying waters (HgT, 0.47 ng L^{-1} ; MeHg, 0.006 ng L^{-1}). Such results suggest that sedimentary remineralization processes are converting particulate Hg to soluble forms. Porewater HgT was not predictive of MeHg, indicating that several factors (e.g., microbial community composition and activity, sulfate, particle decomposition, sedimentation rate) are likely controlling local MeHg content. Porewater Hg species reached maximum levels near the sediment–water interface (1–3 cm depth), just below the zone of active remineralization and diffusion. Distribution coefficients for HgT and MeHg were lower in sediments ($\log K_d = 3.9 \pm 0.2$ and 2.5 ± 0.2 , respectively) relative to settling particulate matter, indicative of remineralization processes. Such processes likely mobilize Hg(II) and MeHg, and facilitate their transport into aquatic organisms. Measures of $\log K_d$ varied positively with volatile organic matter content (by loss on ignition) in sediment strata (particularly for MeHg ($r^2 = 0.81$)), indicating that organic matter associations (presumably Hg–thiols; ref 39) are to a large extent controlling partitioning. Generally, distribution coefficients for HgT and MeHg in Lake Superior's clay-rich, organic-poor sediments are very low relative to those of other aquatic systems (Table 3), suggesting that Hg is more mobile and prone to re-entering the water column and food webs in Lake Superior than in other aquatic systems. Sediments from Lakes Superior and Michigan deviate from what we consider typical, productive lakes with organic-rich sediments with $\log K_d$ values for HgT in the range of 4.5–5.5. Although rates of in situ methylation in the deep sediments of Lake Superior appear to be extremely small (14), we predict that the MeHg produced has a greater chance for transport and biological incorporation.

Mass Balance. A preliminary mass balance for HgT and MeHg was constructed for Lake Superior (Figure 4), based upon observed means of particulate and raw water speciation, best estimates from the literature, and by closing the budget with the least-constrained parameter. Considering the lack of constraint on several model terms, we view this mass balance as a tool to aid in defining future research efforts within the basin. The model incorporates the following input and sink terms.

TABLE 2. Hg Speciation in Lake Superior Sediment Cores, August 2000^a

station	section depth cm	part HgT ng g ⁻¹ dw	porewater HgT ng L ⁻¹	HgT log Kd L kg ⁻¹	part MeHg ng g ⁻¹ dw	porewater MeHg ng L ⁻¹	MeHg log Kd L kg ⁻¹
2	0-1	117			0.27 (0.26, 0.29)		
	0-2	128				0.23	
	2-4	128				0.14	
	4-6	130					
	6-8	42.2					
	8-10	94.6					
4	0-1	91.3	5.0	4.3	0.19 ± 0.01	0.82	2.4
	1-2	30.0	32.1	3.0		a	
	2-3	58.0	143	2.6		0.35	
	3-4	48.8 (48, 50)	8.0	3.8		2.23	
6	0-1	61.4			0.14		
	0-2	43.0				0.15	
	2-4	45.6				0.18	
	4-6	43.8					
	6-8	56.6					
	8-10	49.3					
10	0-1	82.5			0.27 (0.25, 0.29)		
	0-2	92.4				0.24	
	2-4	123				0.18	
	4-6	122				0.28	
15	0-1	209	7.7	4.4	0.43 (0.38, 0.47)	0.24	3.2
	1-2	213	5.4	4.5		0.27	
	2-3	243	26.2	3.9		0.53	
	3-4	222 (151, 293)	26.4	3.9		0.17	
	4-6	102 (98, 107)	85.9	3.1		0.34	
	6-8	62.5	26.5	3.4		0.27	
	8-10	51.9					
17	0-1	30.9			0.31 (0.30, 0.32)	0.13	
19	0-1	102				0.21	
	0-2	93.3				0.11	
	2-4	84.0				0.10	
	4-6	125				0.07	
	6-8	108				0.04	
	8-10	68.1				0.04	
20	0-1	25.8 (16, 36)	7.2	3.6	0.04	0.31	2.1
	0-2	16.1				0.11	
	2-3	19.2	18.6	3.0		0.02 ^a	
	3-4	27.8	26.2	3.0			
	4-6	33.9					
	6-8	27.8					
	8-10	19.0					
21	0-1	128	21.2	3.8	0.30 (0.30, 0.31)	0.47	2.8
	0-2	71.6	24.0	3.5		1.17	
	2-3	46.7				2.54	
	3-4	114	38.7	3.5		0.37	
	4-6	20.7					
	6-8	15.1					
	8-10	32.8					
22	Ponar grab	105			0.42		

^a Below detection limit. 0-1 cm Core sections were analyzed separately from 0-2 cm sections for Stations 2, 6, 10, 19, 20, and 21. (#) = range of duplicate samples.

Atmosphere. Deposition of HgT was estimated assuming a wet plus dry flux of $9 \mu\text{g m}^{-2} \text{yr}^{-1}$, based upon the work of Fitzgerald et al. (10) at a site in northern Wisconsin. Atmospheric supply of MeHg was based upon 3 years of measurement from three sites with the Lake Superior basin, with a mean wet deposition concentration of 0.15 ng L^{-1} (13, 14).

Tributaries. HgT and MeHg loads were based upon the results of Babiarz (13), who measured riverine flows and Hg species concentrations on several U. S. tributaries, with scaling to the entire lake based upon flow and geographic information system (GIS) data.

Remineralization/Methylation. These terms are based upon passive diffusion from measured porewaters, applying a diffusion coefficient of $2 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ to a gradient of HgT and MeHg across the sediment-water interface (40). Although this term lacks constraint relative to the others, it is likely a lower bound to sedimentary input; this is due in part

to ignoring the role of benthic infauna and local eddy diffusivity. While our measurements of porewater Hg gradients cannot distinguish between remineralization of settling material and in situ methylation, the low experimental methylation rates observed with stable isotopic techniques lead us to believe that in situ production is small relative to remineralization in offshore sediments (14).

Groundwater. HgT and MeHg were estimated with a mean value of $550 \text{ m}^3 \text{ km shoreline}^{-1} \text{ d}^{-1}$, based upon modeling of groundwater flow into Lake Michigan by Sellinger et al. (41). These water fluxes were multiplied by 5.0 ng L^{-1} for HgT and 0.2 ng L^{-1} for MeHg, which were observed in subsurface porewaters during the August 2000 cruise. Considerable uncertainty exists for this value as no data are currently available for inputs to Lake Superior, and because of differences in groundwater flow estimation techniques.

Evasion. Evasion flux was used to close the HgT budget, as constraint of air-water fluxes using wind-driven gas-

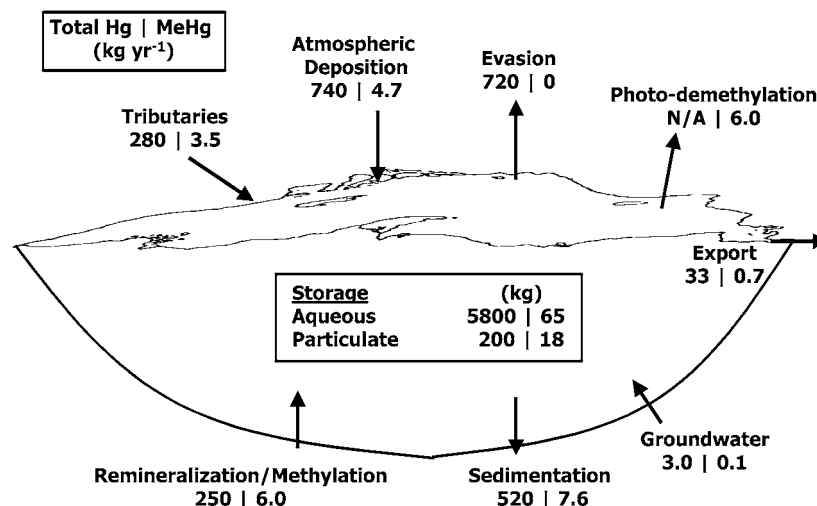


FIGURE 4. Initial estimate of mass balance for HgT and MeHg in Lake Superior, with transport in kg/yr. N/A = not applicable, as we assume that demethylation does not deplete HgT.

TABLE 3. Summary of Mean Porewater Distribution Coefficients for HgT and MeHg

system	HgT log Kd L kg ⁻¹	MeHg log Kd L kg ⁻¹	reference
Lake Superior	3.9	2.5	this study
Lake Superior	2.7		19 ^a
Lake Michigan	3.5		19 ^a
Little Rock, WI	3.8		28
Palette, WI	4.5	4.0	J. Hurley, unpub. data
St. Laurence, QC	4.4		44
Laurentian Trough, QC	4.8		45
Lavaca Bay, TX	4.9	2.7	46
Lake Onandaga, NY	5.9	3.5	47

^a Estimated from surficial samples in published figures.

exchange models supply the greatest variability in estimation (on the order of $\pm 30\%$; ref 25). Nevertheless, the value employed (720 kg yr^{-1}) is similar to that calculated by a gas-exchange model based on measured wind speed and other parameters (600 kg yr^{-1} ; mean DGM = 0.02 ng L^{-1} , mean water temp. = 7°C , atmospheric Hg^0 = 1.7 ng m^{-3} , and mean square of wind speed = $20 \text{ m}^2 \text{ s}^{-2}$; ref 25).

Photodemethylation. The photodemethylation rate was based upon a MeHg demethylation conversion rate of $2\% \text{ d}^{-1}$ in incubated samples from high-altitude lakes (36), and applied to an assumed 1-m surficial reaction depth at the air–water interface. This value is not well constrained, and variables such as depth of light penetration and suspended particulate matter content are likely key rate-determining factors.

Export. Export of HgT to Lake Huron was estimated with mean data for the St. Mary's River at Sault Ste. Marie, MI ($2130 \text{ m}^3 \text{ s}^{-1}$; ref 42) and the mean aqueous HgT and MeHg concentrations (0.50 and 0.01 ng L^{-1} , respectively).

Sedimentation. The HgT sedimentation flux ($17 \text{ ng m}^{-2} \text{ d}^{-1}$; 520 kg yr^{-1}) was calculated by applying the mean HgT concentration in seston (43 ng g^{-1}) to an estimate of the mean offshore sedimentation rate, based upon sediment trap collections ($0.4 \text{ g m}^{-2} \text{ d}^{-1}$; ref 17). Fluxes calculated by Rossman (4), who determined sedimentation fluxes with stratigraphic analysis of sediment cores coupled with ^{137}Cs dating, suggest a much larger HgT flux that our budget inputs cannot support ($88 \text{ ng m}^{-2} \text{ d}^{-1}$; 2620 kg yr^{-1}). This difference is substantial, and likely arises from the following: (1) greater

than 50% of the sediment originates from erosion, focusing, slumping, and transport of shoreline material rather than vertical sedimentation (43), much of which is not included in sediment trap collections, and (2) internal sources that are not accounted for, such as stamp sand mineral deposits and localized industrial discharges. Although it is unclear which sedimentation value is most appropriate, the trap material is likely more recyclable to the upper reaches of the offshore water column, and consequently, more prone to evasion. We used sedimentation flux to “close” the MeHg budget, as other terms were more tightly constrained. This term is considered gross transport, as some MeHg remineralizes and diffuses back into the water column.

We estimated that the water column holds approximately 6 metric tons of Hg, with approximately 1% as MeHg (we do not present data for the contribution of MeHg from fish biomass to the mass balance, but we assume that this is an important compartment for storage within the lake). Particulate material was enriched in MeHg relative to the aqueous phase (in terms of %HgT), potentially due to the contributions of efficient scavenging to biota and photodemethylation of the aqueous phase.

Our preliminary mass balance indicates that atmospheric deposition dominated the supply of HgT (primarily inorganic Hg) to the lake, followed by tributary inputs and that of particulate remineralization—perhaps not surprising in a large lake with a relatively small watershed area/lake area ratio. Rossman (4) estimates that only 38% of the Hg flux to sediments is derived from atmospheric deposition, which is far less than our estimate of 58%. Again, this is likely due to differences in accounting for vertical sediment trap derived particles versus horizontal focusing and shoreline erosion. Evasion of Hg^0 was the principal removal term, on the same order as atmospheric deposition and sedimentation. Approximately half of the HgT in particulate matter reaching the sediments was remineralized, and export and groundwater terms were generally much smaller. Estimation of lake HgT storage results in a residence time (pool size/removal rate) for HgT of 4.6 years in the aqueous phase, and 0.4 years in the particulate phase if only sedimentation is considered.

Sources of MeHg to the lake are more evenly divided between the atmosphere, tributaries, groundwater, remineralization, and in situ methylation, whereas sedimentation and photodemethylation were the dominant removal processes. We suggest that in-lake methylation occurred in the warmer, shallow sediments, whereas tributary MeHg was primarily supplied during the Spring. Recent studies have

shown that planktonic MeHg content peaks during the Spring period in Lake Superior (22). Such observations imply that tributary MeHg is more available to the planktonic food web than is MeHg from in situ sources, though the benthic food web has yet to be thoroughly studied with regards to bioaccumulation. Estimates of MeHg residence time are 4.5 years for aqueous MeHg and 2.4 years for particulate MeHg, based only upon the sedimentation term.

Lake Superior is a unique freshwater system in that it shares many features with marine waters, including low aqueous and particulate Hg species concentrations, low sedimentary organic content, and resultant enhanced partitioning into the dissolved phase. We must consider these aspects, as resource managers typically utilize data from smaller, much more productive lakes for policy and decision making with regards to mercury.

Although our data indicate that both HgT and MeHg concentrations are low, fish consumption advisories have been issued for Lake Superior waters. Sources of bioaccumulative MeHg are diffuse in the open waters—yet in nearshore regions, tributary mixing zones can expose biota to MeHg concentrations that are orders of magnitude greater. For these reasons, we are focusing additional research on bioaccumulation processes in tributary mixing zones (6).

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